Supporting Information

Propagating Concentration Polarization at Microchannel-Nanochannel Interfaces
Part II. Numerical and Experimental Study

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This document contains the following supporting information for the article:

- Extended description of the channel conditioning procedure used in this study
- Description of anomalous shock propagation behaviors
- Figure S-1: Colored spatio-temporal plots showing the effects of increasing current density on measured, propagating enrichment and depletion fronts.
- Figure S-2: Colored spatio-temporal plots showing measurements of anomalous propagating enrichment and depletion front behaviors.
Channel Conditioning Procedure
Before and after each day of experiments, we cleaned our channels using DI water via pressure-driven flow (~1 atm). After cleaning, we flushed the microchannel-nanochannel devices by pressure driven flow (~1 atm) for 40 min with the electrolyte of interest, then allowed them to come to equilibrium under no-flow conditions for 5 min before the next experiment. Experiments were typically conducted on any given channel over a period of ~10 days, and nine were fabricated and used for the study. We found some channels degraded over time, making reproducible experiments difficult. To help validate reproducibility, we measured channel current at the start of each day; and retained channels for additional experiments if measured current was within about 20% of the average current measured at a given electrolyte concentration. We hypothesize that this gradual degradation of performance may be due to long-term electrochemical changes of the surface.1

Anomalous Shock Propagation Behaviors
We observed oscillating enrichment region concentration and enrichment/depletion shock velocities in approximately 10 out of 81 experiments at the highest (1 mM) Alexa Fluor 488 concentration and highest applied currents (2 and 4 nA) (see Figure S-2a). Also, for several conditions, a front was observed to move into the microchannel from either the anode or cathode side well. When this front intersected the depletion or enrichment shock, respectively, the shock velocity abruptly changed (see Figure S-2c and S-2d). We hypothesize that this is due to a propagation of chemical disturbances from the reservoir (which is exposed to the room air and in which electrochemical reactions occur). The reported enrichment region concentration and shock velocities are measured before the onset of oscillations or the abrupt shift in shock velocity.

References
Figure S-1. Measured spatiotemporal plots showing the effect of increasing current density. (a) 50 pA, (b) 200 pA, (c) 800 pA, (d) 1.4 nA, (e) 2 nA, (f) 4 nA. The enrichment and depletion front velocities were approximately linear with applied current, as predicted by theory and shown in Figure 6. These images also show some other features of high current realizations including curved initial front velocities (d, f) and a high concentration intersecting the depletion region ((f), also discussed in Figure S-2). Images show measured, width-averaged concentration as a function of axial position and time. Red indicates high concentration, blue indicates low concentration. We used a 100 μm long 50 nm deep nanochannel in series with two 1 μm deep microchannels. The total system length was 10 mm, and all channels were 20 μm wide. The nanochannel is visible at around x = 1200 μm. The system was initially filled with 1 mM Alexa Fluor 488 dye by pressure driven flow.
Figure S-2. Measured spatiotemporal plots showing several anomalous behaviors of propagating CP fronts. (a) Banded appearance of enrichment fronts accompanied by fluctuating depletion shock velocity for (high) 2 nA applied current and 1 mM initial concentration. Note that equation 8 of Part II predicts that a variation in the depletion front velocity should cause a change in the enrichment region concentration, as shown here. (b) Transient, curved fronts for 800 pA applied current and an initial concentration of 50 μM. As the enrichment and depletion shock velocities changed over time the enrichment region concentration also varied slowly. This may be due to changing conditions inside the nanochannel. Fronts from the (c) cathode and (d) anode side wells intersected the growing enrichment and depletion regions, respectively. The conditions for these experiments were (c) 1.4 nA, 100 μM, (d) 2 nA, 1 mM. In (c) a low concentration front intersects the enrichment region at approximately x = 2200 μm and t = 45 s. In (d) a high concentration front intersects the depletion region at approximately x = 400 μm and t = 45 s. In all images red indicates high concentration, blue indicates low concentration. For all experiments shown here we used a 100 μm long 50 nm deep nanochannel in series with two 1 μm deep microchannels. The total system length was 10 mm, and all channels were 20 μm wide. The nanochannel is visible at around x = 1200 μm. The system was initially filled with a uniform concentration of Alexa Fluor 488 dye by pressure driven flow.